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DEFENCE RESEARCH ESTABLISHMENT
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IMPROVED PROCESS FOR THE SYNTHESIS OF SECOND GENERATION BRANCHED GAP

by

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ABSTRACT

Second generation branched Glycidyl Azide Polymer (GAP) is prepared according to a novel single-step degradation process developed at DREV by reacting a high molecular weight (MW ~ 10^6) commercial rubbery polyepichlorohydrin (PECH) with sodium azide and a basic cleaving agent in the presence of a polyol for a few hours at elevated temperature in a polar organic solvent. However, in this process, the cleaving agent and/or the polyol are optional. For reactions involving a cleaving agent, the hydroxyl functionality of the GAP product is between 2 and 10 and the MW may be controlled and predetermined in the MW range 1000-40,000 by varying the concentration of the cleaving agent in the reaction mixture. For reactions without a cleaving agent, the MW of the product is between 40,000 and 200,000 and the functionality is equal to, or above 10. The effect of some reaction parameters on the properties (MW, viscosity, hydroxyl content and functionality) of the branched GAP product was studied. The synthesis parameters investigated are the reaction time and temperature, the type and concentration of the cleaving agent, polyol and solvent as well as the sequence of addition of the reactants. Branched GAP with relatively low MW (~ 10,000) and viscosity (~ 40,000 cP at 25°C) can be synthesized in about 5 h at 120°C in dimethyl sulfoxide (DMSO) and the product thus obtained has a relatively higher hydroxyl content than its counterpart prepared in dimethyl acetamide (DMA) in similar experimental conditions.

RÉSUMÉ

Le polyazoture de glycidyle (PAG) ramifié de seconde génération est préparé en une seule étape selon un nouveau procédé de dégradation développé au CRDV. Ce procédé implique la réaction d'un polyépichlorohydrine (PECH) commercial caoutchouteux de masse moléculaire élevée (MM ~ 10^6) avec l'azoture de sodium et un agent de clivage basique en présence de polyol dans un solvant organique polaire durant quelques heures à température élevée. Cependant, dans ce procédé, l'agent de clivage et/ou le polyol sont optionnels. Pour les réactions utilisant un agent de clivage, la fonctionnalité en hydroxyle du produit PAG est entre 2 et 10 et la MM peut être contrôlée et prédéterminée dans le domaine de MM entre 1000 et 40,000 en faisant varier la concentration de l'agent de clivage dans le mélange réactionnel. Pour les réactions sans agent de clivage, la MM du produit se situe entre 40,000 et 200,000 et la fonctionnalité est égale ou supérieure à 10. On a étudié l'effet de certains paramètres réactionnels sur les propriétés (MM, viscosité, concentration hydroxyle et fonctionnalité) du produit PAG ramifié. Les paramètres de synthèse examinés sont le temps et la température de réaction, le type et la concentration de l'agent de clivage, du polyol et du solvant ainsi que l'ordre d'ajout des réactifs. Le PAG ramifié de MM (~ 10,000) et de viscosité (40,000 cP à 25°C) relativement faibles peut être synthétisé dans le sulfoxyde de diméthyle (DMSO) à 120°C en environ 5 h et le produit ainsi obtenu a une concentration hydroxyle relativement plus élevée que le produit équivalent préparé dans le diméthyle d'acétamide (DMA) dans des conditions expérimentales similaires.

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EXECUTIVE SUMMARY

Glycidyl Azide Polymer (GAP) is a potential energetic binder for rocket propellants with reduced smoke and low vulnerability as well as for insensitive composite explosives and gun propellants. For these reasons, GAP is considered as an attractive substitute for the inert hydroxy-terminated polybutadiene conventional binder currently used in energetic formulations such as the CRV-7 rocket motor.

GAP currently produced in the USA is relatively expensive and is prepared according to a two-step process involving two distinct chemical reactions. In 1987, a process was discovered at DREV for the preparation in a single step of first generation Canadian branched GAP by reacting a polyepichlorohydrin (PECH) rubber with epichlorohydrin (ECH) monomer and sodium azide.

The purpose of this study is to describe an improved process developed and patented recently by DREV for the preparation of second generation branched GAP in one step but without the addition of an epoxide monomer such as ECH. The chemical reaction has been simplified in this novel process which involves both the degradation and azidation of a cheap commercial rubbery PECH with sodium azide in the presence of a base (optional) and a polyol (optional) for a few hours at elevated temperature. Besides, this process is versatile since the MW, viscosity and hydroxyl content of the product may be controlled by varying the relative proportions of the reactants. It is another object of this report to study the effect of some reaction parameters on the properties of second generation branched GAP obtained according to this novel degradation process.

The technology of this process has been transferred to ICI Explosives Canada under the Defence Industrial Research (DIR) Program to design and build a pilot plant to produce development quantities of branched GAP for testing, to select suitable industrial equipment and to obtain a reliable estimate about the cost of GAP manufacturing. A pilot plant was built at McMasterville with a capacity of 25 kg per week and has been producing since 1993 batches of second generation branched GAP with good properties.

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NOMENCLATURE

$(CH_3)_3COK$	potassium ter-butoxide
CH_3OLi	lithium methoxide
CH_3ONa	sodium methoxide
C_2H_5ONa	sodium ethoxide
DMA	dimethyl acetamide
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
DPE	di-pentaerythritol
ECH	epichlorohydrin
EG	ethylene glycol
f	hydroxyl functionality (average number of OH groups per molecule)
GAP	glycidyl azide polymer
GPC	gel permeation chromatography
HT	hexanetriol
IR	infrared
meq	number of OH milliequivalents
Me	hydroxyl equivalent weight
M_{GAP}, M_{PS}	molecular weight of branched GAP and polystyrene, respectively
M_N, M_W	number and weight average molecular weight, respectively
MW	molecular weight
NaN_3	sodium azide
NaOH	sodium hydroxide
NMP	N-methyl pyrrolidinone
NMR	nuclear magnetic resonance
[OH]	hydroxyl concentration in the polymer expressed in meq/g.
PE	pentaerythritol
PECH	polyepichlorohydrin
PEG	polyethylene glycol
PS	polystyrene

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PVA	polyvinyl alcohol
T	absolute temperature
THF	tetrahydrofuran
TMP	trimethylol propane
η	absolute viscosity

1.0 INTRODUCTION

Glycidyl Azide Polymer (GAP) is a hydroxy-terminated aliphatic polyether containing alkyl azide groups which could be used as an energetic binder in low-smoke solid rocket propellants, composite explosives, gun propellants and pyrotechnics to enhance the performance and stability, reduce the vulnerability and improve the physicochemical properties of the energetic formulations.

GAP with molecular weight (MW 1000 - 6000) is currently produced in the USA (Refs. 1-5) according to a two-step process which requires two distinct reactions (polymerization and azidation). GAP of low MW (approx. 500), which could be used mainly as an energetic plasticizer, can be prepared through a single-step process (Refs. 6-9) developed at DREV. Methods for the synthesis of GAP-Azide plasticizer (Ref. 10) and linear GAP with increased functionality (Refs. 11-12) have also been developed at DREV.

Branched GAP (first generation) with variable MW (500 - 40,000) can also be prepared directly through a degradation process developed at DREV (Refs. 13-18) by reacting a high MW rubbery polyepichlorohydrin (PECH) with the epichlorohydrin (ECH) monomer and NaN_3.

Recently, a novel degradation process was developed at DREV (Refs. 19-21) for the preparation of second generation branched GAP with controlled and variable MW (1000 - 200,000), but without using any epoxide monomer such as ECH in the reaction. This process involves the single-step reaction of a high MW solid rubbery PECH with NaN_3 in the presence of a basic cleaving agent and a polyol in a suitable solvent at elevated temperature; the cleaving agent and/or the polyol are optional. The MW, viscosity, equivalent weight and hydroxyl functionality of the branched GAP

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product can be controlled and predetermined by varying the concentration of the reactants. The scale-up of this process has been achieved at the DREV Experimental Complex (Ref. 22) as well as at the McMasterville Technical Center of ICI Explosives Canada under a Defence Industrial Research (DIR) Project (Refs. 23-26). The purpose of this report is to describe the method of synthesis and the effect of the reaction parameters on the properties of second generation branched GAP prepared according to this improved degradation process.

This work was performed at DREV between September 1989 and May 1994 under PSC 32C, Rockets and Missiles.

2.0 EXPERIMENTAL

2.1 The Improved Degradation Process

Second generation branched GAP is obtained according to an improved degradation process which does not require the use of ECH in the reaction. Branched GAP with predetermined and variable MW (1000 - 200,000) is prepared in a single step by the reaction of a very high MW rubbery PECH with NaN_3 in the presence of a basic cleaving agent and a polyol in a polar organic solvent at elevated temperature. However, in this process the polyol and/or the basic cleaving agent are optional.

The starting PECH reactant mainly used in this study is a relatively cheap commercial solid rubber (Hydrin H45) manufactured by B.F. Goodrich (ZEON CHEMICALS) with a weight average molecular weight (M_W) of 800,000 and a number average molecular weight (M_N) of 280,000.

The process may be conducted at any temperature above 70°C. Generally, temperatures in the range 90°C to 120°C are used; a temperature of 120°C being preferred. The reaction time is generally between 5 and 32 hours, depending on the chosen synthesis parameters and the required specifications for the branched GAP product.

The solvents used in this process must dissolve the rubbery PECH and also sodium azide, the cleaving agent and the polyol, in order to achieve both the degradation and azidation reactions. The suitable solvents include polar organic solvents such as dimethyl sulfoxide (DMSO), dimethyl acetamide(DMA), dimethyl formamide (DMF) and N-Methyl Pyrrolidinone (NMP). Mixtures of different solvents can also be used in the synthesis process.

The basic cleaving agent is mainly used to control and further reduce the MW of the branched GAP product. The use of a cleaving agent increases the degradation rate and thus makes possible the MW reduction in a more extensive manner. The MW of the product can be adjusted to the desired value by varying the cleaving agent concentration in the reaction mixture. When the cleaving agent is used in the reaction, the MW varies within the range 1000-40,000 and the hydroxyl functionality varies between 2 to 10. When the reaction is carried out without a cleaving agent, the MW of the product varies within the range 40,000-200,000 with a hydroxyl functionality equal to or greater than 10. The cleaving agents investigated in this study are lithium methoxide (CH_3OLi), sodium methoxide (CH_3ONa), sodium hydroxide (NaOH) pellets, sodium ethoxide (C_2H_5ONa) and potassium ter-butoxide $(CH_3)_3COK$.

The suitable polyols that can be employed in the process are molecules or polymers containing one or many hydroxyl groups. A mixture of two or more polyols

can also be used in this process. The following polyols were investigated in this study: ethylene glycol (EG), glycerol, hexanetriol (HT), trimethylol propane (TMP), pentaerythritol (PE), di-pentaerythritol (DPE), polyethylene glycol (PEG), GAP, sucrose and polyvinyl alcohol (PVA).

2.2 Reaction Mechanism

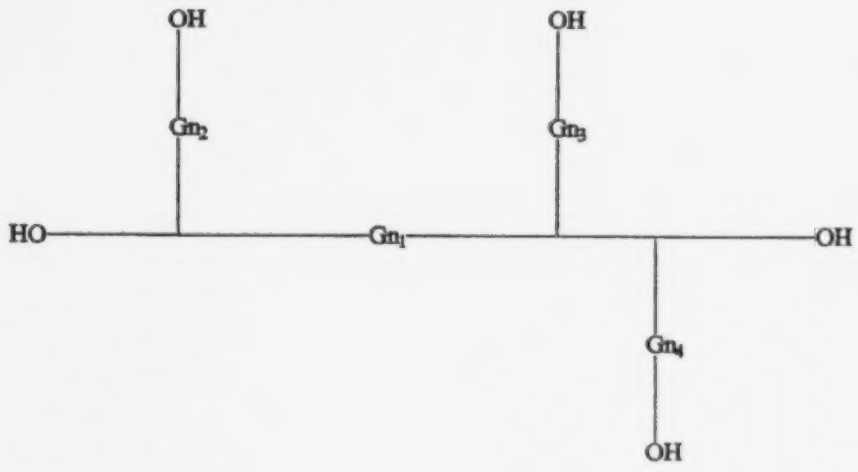
The reaction mechanism is believed to involve:

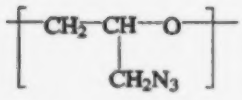
- The degradation and azidation of the high MW rubbery PECH are achieved simultaneously by the combined action of the cleaving agents, the polyol, the azide and elevated temperature; the cleaving agent increasing the degradation rate. The scission occurs at the oxygen bonds and produces long chains of GAP polymers.

- Some of these GAP polymeric chains thus formed are then grafted to the "degraded" rubbery matrix and/or to the polyol present (and thus incorporate the polyol into the GAP product). A portion of the polyol reactant is grafted into the GAP polymer structure and thus becomes part of the molecule.

- Termination reactions occur when the grafting takes place at the oxygen bonds. Branching occurs when the grafting takes place at the alkyl groups involved in the nucleophilic substitution.

The final GAP product thus obtained has a branched structure with terminal OH groups, as shown in the following structural formula:



G = GAP unit 

n = total degree of polymerization
(total number of GAP units)

$$n = (n_1 + n_2 + n_3 + n_4 \ldots\ldots\ldots + n_s) = \sum_{i=1}^{s} n_i$$

n_1 = number of GAP units in segment 1

n_2 = number of GAP units in segment 2

n_s = number of GAP units in segment s

s = total number of segments in the molecule.

for reactions involving a cleaving agent:

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$10 \leq n \leq 400$, $1000 \leq MW \leq 40{,}000$

$2 \leq$ functionality ≤ 10

for reactions without a cleaving agent:

$400 \leq n \leq 2000$, $40{,}000 \leq MW \leq 200{,}000$

functionality ≥ 10

2.3 Methods for the Preparation of Second Generation Branched GAP

Since the polyol and/or the basic cleaving agent are optional, the degradation process can be achieved consequently with three different methods.

2.3.1 Method A

Branched GAP is prepared in a single step according to the following chemical reaction which involves four reactants:

PECH + NaN_3 + Cleaving Agent + Polyol ⟶ Branched GAP

This method will be the main subject of this report.

2.3.2 Method B

This method is similar to method A, except that the polyol is omitted. Thus the reaction system comprises the following three reactants:

PECH + NaN_3 + Cleaving Agent ⟶ Branched GAP

Since the polyol is not included in the reaction, the branched GAP product thus obtained will be different from the one produced according to Method A in terms of MW viscosity, hydroxyl functionality and distribution of OH functionality. The properties of some branched GAP products obtained with Method B are presented in another report (Ref. 27).

Since the cleaving agent is used in both Methods A and B, branched GAP obtained with these two methods will have consequently a MW between 1000 and 40,000 and a hydroxyl functionality of 2-10.

2.3.3 Method C

This method is similar to methods A or B, except that the cleaving agent is omitted. This method involves 2 or 3 reactants, depending on whether a polyol is included or not in the reaction mixture. Branched GAP is prepared in Method C according to the following chemical reaction:

PECH + NaN_3 + Polyol (optional) ⟶ Branched GAP

Since the basic cleaving agent is not used in the reaction, the branched GAP product thus obtained will have a relatively higher MW (40,000-200,000) and OH functionality ($\geq$ 10) compared with the products of Methods A and B. The properties of some branched GAP products obtained with Method C are presented in another report (Ref. 27).

2.4 Synthesis of Branched GAP According to Method A

The synthesis of branched GAP according to Method A using CH_3OLi as cleaving agent and TMP as polyol is described in the following example:

The rubbery PECH (20 g) is cut into small pieces and dissolved in DMSO (100 g) at 60°C for overnight (approx. 15 h). In the following morning, the temperature is raised to 120°C and agitation is started. TMP (5.0 g) and NaN_3 (16 g) are then added to the mixture; the weight ratio (NaN_3/PECH = 0.80) used in the reaction is approximately 10 % above the stochiometric amount. After about 15 min, CH_3OLi (0.6 g) is then added to the reaction mixture and the reaction is carried out with agitation at 120°C for about 5 h. The time interval (15 min) between the addition of azide and the cleaving agent is dependent on the reaction temperature; for reactions achieved at 100°C, this interval is approximately 1-2 h. This waiting period between the addition of the reactants as well as the sequence of their addition will be discussed in Section 3.10. Some gelling could occur following the addition of the cleaving agent. The degree of gelling depends on the type of polyol and cleaving agent used and their respective proportions in the reaction mixture; the gel is barely noticeable for low polyol and cleaving agent concentrations. If the gel is formed, it can be dissipated in 15-30 min. by adding more DMSO (50-100 ml) into the reaction mixture. The gel formation can also be prevented by increasing the initial solvent concentration or by reversing the sequence of addition of the reactants. No gelling is generally observed when the initial amount of solvent is doubled or when NaN_3 is added before the cleaving agent.

2.5 Purification of Branched GAP

When the reaction is completed, heating and agitation are stopped and the reaction mixture is allowed to cool. The solid salts (NaCℓ and unreacted NaN_3) are then filtered out and most of the DMSO is evaporated at 60°C under vacuum. The GAP product recovery from this resultant DMSO solution can be obtained by two different procedures: extraction and water precipitation.

2.5.1 Extraction Procedure

Methylene chloride ($MeCℓ_2$) (400 ml) is added to the resultant DMSO solution obtained in Section 2.5, followed by four extractions with (400 ml methanol/400 ml brine) to remove the remaining DMSO, TMP and salts. The number of extractions is dependent on the reaction solvent; DMSO is much easier to extract compared, for instance, with DMA. For DMSO, four extractions are adequate, whereas for DMA, six extractions are required to remove completely the residual solvent from the GAP product. The $MeCℓ_2$ solution is dried over anhydrous magnesium sulfate; after salt filtration, the $MeCℓ_2$ is then evaporated under vacuum (60°C, 1 h) to yield 20.3 g (95 %) of branched GAP: a viscous liquid with a light yellow colour and a density of 1.3 g/ml.

The extraction technique makes it possible to obtain high polymer yields (about 95 %), but requires large volumes of $MeCℓ_2$, methanol and brine. For this reason, the extraction procedure is useful for small laboratory scale but is not practical for big industrial scale.

2.5.2 Water Precipitation Procedure

Water (2 L) is gradually added to the resultant DMSO solution (obtained in Section 2.5) until a slight turbidity develops and polymer precipitation occurs. The solution is stirred slowly during precipitation. The precipitated phase is then allowed to settle and the supernatant aqueous phase is removed; this aqueous solution contains water, DMSO, TMP and salts. This operation of water addition is repeated three times followed by evaporation (60°C, 1 h) under vacuum to recover 18.2 g (85 %) of branched GAP product.

Methylene Chloride, methanol and brine are not needed in the water precipitation technique which gives nevertheless acceptable polymer yield (about 85 %). This water precipitation procedure is very practical for large industrial scale and has been applied for the purification of branched GAP at the pilot plant of ICI in McMasterville.

The comparison of properties of branched GAP samples purified according to the extraction and water precipitation procedures are presented in another report (Ref. 27). The purification of branched GAP by chromatography columns containing different adsorbents has also been investigated and the results of this study are also presented in that other report (Ref. 27).

2.6 Characterization of Branched GAP

2.6.1 Azide Conversion

The azide conversion of the branched GAP product was determined by ^{13}C NMR according to the method reported in Ref. 28 and by elemental analysis with a

Perkin-Elmer instrument (model 2400 CHNO). The elemental analysis yielded: C (37.0), H (5.0), N (42.0), O (16.0) wt % and confirmed that quantitative conversion of PECH to GAP was achieved.

2.6.2 Gel Permeation Chromatography

The characterization of branched GAP by gel permeation chromatography (GPC) was achieved with a Waters system comprising an automatic injector (Model 712), a pump (Model 590) and a refractive index detector (Model 410). The chromatograph was operating at 25°C using stabilized tetrahydrofuran (THF) as a solvent with a flow rate of 1 ml/min. Four Waters Ultrastyragel columns were used with median porosities of 10^5, 10^4, 500 and 100 Å.

The weight average molecular weight (M_W) and the number average molecular weight (M_N) of branched GAP were determined by GPC according to the Universal Calibration Method based on the hydrodynamic volume concept reported in Ref. 29. The GPC calibration was performed with polystyrene (PS) standards. For a given elution volume, the following relation was established for the conversion of PS MW to branched GAP MW:

$$M_{GAP} = 0.51\ M_{PS}^{1.075}$$

2.6.3 Hydroxyl Equivalent Weight of Branched GAP

The hydroxyl equivalent weight (M_e) for all the branched GAP samples studied was determined according to the infrared absorption spectroscopy method described in Ref. 30. The M_e values for a few samples were also measured by NMR

(Ref. 31) and found in agreement with the values obtained by IR. The hydroxyl functionality (f) of branched GAP was calculated from the ratio (M_N/M_e).

2.6.4 Viscosity of Branched GAP

The absolute viscosity (η) measurements of second generation branched GAP were determined with a Haake Rotovisko Rotational Viscometer using a cone and plate system at different temperatures and shear rates. The viscosity of second generation branched GAP varied with temperature (T) according to the following empirical relation:

$$\frac{d \log \eta}{d(1/T)} = 3.2X10^3 \quad cP.\ K \qquad (1)$$

This relation (determined in the temperature range 25-60°C) is similar to the one established for first generation branched GAP in Ref. 16. Second generation branched GAP had a Newtonian behavior in the range of shear rate investigated (below 20 s^{-1}) since its viscosity did not vary with shear rate.

3.0 RESULTS AND DISCUSSION

The reaction parameters selected for the synthesis of second generation branched GAP have a significant effect on the product properties and characteristics such as the MW, viscosity, OH Equivalent weight, functionality etc. The correlation between the MW of the starting PECH material and the MW of the branched GAP product was discussed in a previous report (Ref. 16); high MW reactant PECH rubbers will generally yield GAP products with relatively high MW compared with those produced from the degradation of low MW PECH rubbers.

The reaction parameters investigated in this study are the reaction time and temperature, the type and concentration of the cleaving agent, polyol and solvent as well as the sequence of addition of the reactants. Since these synthesis parameters are interdependent, the effect of a specific parameter can only be studied if the other reaction conditions are uniform.

In this report, the proportions of the reactants relative to PECH are expressed as weight ratio, except in Section 3.3 and Table III where molar ratios were used for the cleaving agents concentrations in order to assess and compare the chain scission efficiency of various cleaving agents with different MW.

3.1 Effect of Reaction Time

The effect of reaction time on the MW of the branched GAP product was investigated in three different solvents (DMSO, DMA, DMF), as reported in Table I. All the samples were prepared at 120°C using CH_3OLi as the cleaving agent and glycerol as the polyol with similar weight ratios for the reactants: (CH_3OLi/PECH) = 0.041 and (glycerol/PECH) = 0.25.

Samples E 148 (M_w = 12,000), E 156 (M_w = 8500) and E 158 (M_w = 7000) were obtained in DMSO after respectively 5 h, 16 h and 32 h. Samples E 174 (M_w = 11,500) and N 33 (M_w = 9000) were obtained in DMA after 5 h and 16 h, respectively. Samples E 171 (M_w = 12,000) and E 169-2 (M_w = 9500) were obtained in DMF after 5 h and 16 h, respectively. The results found for all these samples prepared at different reaction times indicate that, in a given solvent and at a fixed reaction temperature and polyol and cleaving agent concentrations, the MW of the product decreases with the reaction time as expected. The effect of the reaction time on the degradation rate will

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become more or less significant depending on other synthesis parameters as will be shown in the next sections.

3.2 Effect of Reaction Temperature

The effect of the reaction temperature on the MW of the branched GAP product was also investigated in different solvents (DMSO, DMA), as reported in Table II. All the samples were prepared with the same polyol concentration: (Glycerol/PECH) = 1.0. The cleaving agent was NaOH for the samples prepared in DMA and CH_3OLi for the samples obtained in DMSO.

Samples E 55 and N 48 were obtained in DMA after 16 h with a similar cleaving agent concentration (NaOH/PECH = 0.05) but were prepared at different reaction temperatures. Sample E 55 (prepared at 100°C) had a higher M_w (43,400) than Sample N 48 (M_w = 14,800) which was prepared at 120°C.

Samples E 241 (M_w = 20,700), E 242 (M_w = 15,500) and N 12 (M_w = 13,500) were obtained in DMSO after 16 h with similar cleaving agent concentration (CH_3OLi/PECH = 0.03) but were prepared respectively at 90°C, 100°C and 120°C. As expected, an increase in the reaction temperature caused an increase in the degradation rate and consequently a reduction in the MW of the GAP product. The results of Samples E 242 and N 12 (prepared with low cleaving agent concentration) indicate that the MW was reduced by about 15 % when the reaction temperature was raised from 100°C to 120°C.

Samples E 130 (M_w = 4800) and E 238 (M_w = 2600) were also obtained in DMSO after 16 h at respectively 100°C and 120°C but with a relatively higher cleaving agent concentration. For a ratio (CH_3OLi/PECH = 0.10) an increase in the

reaction temperature from 100°C to 120°C caused a more significant MW reduction (approx. 85 %).

Samples E 153 (M_w = 6700) and E 131 (M_w = 4700) were also prepared in DMSO at respectively 90°C and 100°C with a high cleaving agent concentration (CH_3OLi/PECH = 0.10) but were obtained after a reaction time of 32 h. The MW was reduced by about 43 % when the reaction temperature was increased from 90°C to 100°C. Nevertheless, at high cleaving agent concentration, no further MW reduction was observed when the reaction time was extended from 16 h to 32 h since Samples E 130 and E 131 (obtained at 100°C after 16 h and 32 h, respectively) have practically the same M_w (about 4700). This is an indication that at high reaction temperature (100°C) and high cleaving agent concentration, most of the chain scission, which causes MW reduction, is occurring in the first 16 h of the reaction. Consequently, at high cleaving agent concentration, the effect of the reaction temperature on the GAP MW is more significant than the effect of reaction time.

3.3 Effect of Cleaving Agent Type

The effect of the type of cleaving agent used in the reaction on the MW of the branched GAP product was investigated in three different solvents (DMSO, DMA, DMF) and the results are presented in Table III. The following basic cleaving agents were tested: CH_3OLi (MW = 38), NaOH (MW = 40), CH_3ONa(MW = 54), C_2H_5ONa(MW = 68) and K Ter Butoxide (MW = 112). These cleaving agents, which had different MW, were used in the reactions in similar molar concentrations (rather than weight concentrations) in order to assess and compare their respective chain scission efficiencies.

The molar ratio of cleaving agent relative to PECH was calculated from the following expression:

$$[\text{cleaving agent}] = \frac{W_2 M_1}{W_1 M_2} \qquad (2)$$

where W_1 and W_2 are respectively the weight of PECH and cleaving agent used in the reaction, M_1 and M_2 are respectively the MW of PECH and cleaving agent.

The branched GAP samples prepared in DMSO and DMA were obtained after 16 h at 120°C with (TMP/PECH) = 0.25, whereas the samples prepared in DMF were obtained after 32 h at 100°C with (EG/PECH) = 1.0.

Samples N 65 (M_w = 9535), N 146 (M_w = 9219) and E 211 (M_w = 19,000) were obtained in DMSO using respectively CH_3OLi, NaOH and CH_3ONa as cleaving agents. Samples N 65 and N 146 had approximately the same MW, whereas Sample E 211 had a higher MW even though it was prepared with a higher cleaving agent concentration. Consequently, CH_3OLi and NaOH are more effective than CH_3ONa for chain cleaving and MW reduction in DMSO.

Samples N 55 (M_w = 9100), E 178 (M_w = 15,400) and N 147 (M_w = 55,100) were prepared in DMA using respectively CH_3OLi, NaOH and CH_3ONa as cleaving agents in similar molar ratio. The results in DMA indicate that CH_3OLi was the most efficient cleaving agent followed by NaOH, whereas CH_3ONa (as in DMSO) was the least effective cleaving agent.

Samples E 27 (M_w = 10,700), E 24 (M_w = 13,000) and E 25 (M_w = 28,000) were obtained in DMF using respectively NaOH, K Ter Butoxide and C_2H_5ONa as

cleaving agents; in DMF, the molar ratio (0.35) used for the cleaving agent was relatively higher than the ratio (0.070 - 0.10) used in DMSO and DMA. The results in DMF show that NaOH and K Ter Butoxide have about the same efficiency, whereas C_2H_5ONa was the least effective cleaving agent.

3.4 Effect of Cleaving Agent Concentration

The effect of the cleaving agent concentration on the MW and viscosity of the resulting branched GAP product was investigated under different reaction conditions, as reported in Table IV. The GAP samples were prepared in DMSO, DMA and a mixture (70 % DMSO - 30 % NMP) using CH_3OLi as the cleaving agent at reaction temperatures of 90-120°C and reaction times between 5 and 32 h. The weight ratio (Polyol/PECH) used in the reactions was 0.5-1.0 for glycerol and EG and 0.25 for TMP.

The variation of M_w versus the cleaving agent concentration was also plotted in Fig. 1 for the samples obtained in the system DMSO/glycerol at three different reaction temperatures (90°C, 100°C, 120°C). As shown in Table IV and in Fig. 1, the values of M_w for the branched GAP samples are generally reduced by increasing the weight ratio CH_3OLi/PECH used in the reaction mixture. At low cleaving agent concentrations, the MW decreases gradually, through chain scission, until it reaches a minimum value and then as the concentration of the cleaving agent is increased. Furthermore, a reverse phenomenon takes place occasionally and produces, by cross-linking, the opposite effect: a MW increase. This phenomenon was observed for Sample E 139 (prepared in DMSO at 90°C) and for Samples E 72 and E 77 (obtained in DMA at 100°C) when the ratio (CH_3OLi/PECH) exceeded 0.15-0.20. This cross-linking reaction becomes more significant than the degradation reaction at high cleaving agent concentrations which will depend on synthesis parameters such as

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the ingredients types and their relative proportions as well as the reaction time and temperature. The results show that the MW and viscosity of branched GAP can be controlled and predetermined by adjusting the cleaving agent concentration in the reaction mixture (i.e. for a given rubber, solvent, polyol, reaction time and temperature).

The correlation between the cleaving agent concentration and the reaction temperature was studied by comparing the results of branched GAP samples obtained in DMSO at 120°C and 100°C. As shown in Table IV, Sample N 16 (obtained after 5 h at 120°C) had a much lower M_w (12,400) and viscosity (50,000 cP) compared with Sample E 107 (M_w = 33,000, η = 135,000 cP) which was obtained after 16 h at 100°C using the same cleaving agent concentration (CH_3OLi/PECH = 0.03). Consequently, higher reaction temperatures shorten the reaction time and also enable the use of low cleaving agent concentrations to attain the same degradation rate achieved at lower temperatures with higher concentrations. Branched GAP products with relatively low MW and viscosity can therefore be produced in approximately 5 h at 120°C by using a lower proportion of cleaving agent than the one normally used at 100°C. The reduction of the amount of cleaving agent in the reaction has also a significant effect on the thermal properties of the product. Another great advantage of using low cleaving agent concentrations is the enhancement of the thermal stability of the product; the correlation between the synthesis parameters and the vacuum thermal stability of the branched GAP product will be discussed in another report (Ref. 27).

3.5 Effect of Solvent Type on Degradation

The effect of the type of solvent used in the synthesis reaction on the MW of the branched GAP product was investigated in DMSO, DMA and DMF as reported in Table V. The following four systems of polyol/cleaving agent were tested: EG/NaOH, EG/CH_3OLi, glycerol/NaOH and glycerol/CH_3OLi. All the GAP samples

were obtained after 16 h at 120°C with (polyol/PECH) = 0.25 and (cleaving agent/PECH) = 0.043.

As shown in Table V, the samples prepared in DMSO had a much lower MW than the samples obtained in DMA and DMF in all cases. However, in the system (glycerol/CH_3OLi), the results for the three solvents were equivalent: Samples N-09-2 (M_w = 7600), E 175 (M_w = 8400) and E 169 (M_w = 8500) obtained respectively in DMSO, DMA and DMF had practically the same MW. The samples prepared in DMA and DMF had approximately similar MW in all the systems studied except EG/NaOH; in that system Sample E 173 (M_w = 14,300) obtained in DMA had a much lower MW than Sample E 168 (M_w = 62,000) prepared in DMF.

The solubility of the four combinations of (polyol/cleaving agent) investigated seem to be better in DMSO than in DMA or DMF. Consequently, the chain cleavage and MW reduction are achieved more rapidly in DMSO. These conclusions hold evidently for the systems and in the concentration range tested. If, for instance, other co-reagents were used in the reaction and/or the relative proportions of the ingredients were altered, these conclusions could be different.

3.6 Effect of Solvent Concentration on Degradation

The effect of the solvent concentration on the MW of the branched GAP product was studied in DMA at a reaction temperatures of 120°C as reported in Table VI. All the samples were obtained after 16 h with CH_3OLi as the cleaving agent and using EG or glycerol as polyol with a weight ratio (polyol/PECH) = 0.25.

Samples N 36 (M_w = 19,100) and E 244 (M_w = 14,400) were prepared with similar concentrations of cleaving agent (CH_3OLi/PECH = 0.045) and EG but with

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different solvent concentrations. Samples E 175 (M_W = 10,000) and E 243 (M_W = 9000) were also prepared with similar concentrations of cleaving agent (CH_3OLi/PECH = 0.042) and glycerol but with different solvent concentrations. The results found for Samples N 36 and E 244 (obtained with a ratio DMA/PECH of 8 and 16, respectively) as well as for Samples E 175 and E 243 (obtained with a ratio DMA/PECH of 8 and 16, respectively) show that the MW of the product was reduced by about 11-36 % when the solvent proportion was increased in the reaction.

An increase of the DMA proportion in the reaction mixture enhanced the chain scission efficiency of the cleaving agent and thus caused a further reduction in the MW of the GAP product. Consequently, the MW reduction, caused by an increase in the solvent proportion, is largely dependent on the type and concentration of the cleaving agent used in the reaction.

3.7 Solvent Effect on Hydroxyl Content in Product

The solvent effect on the hydroxyl content in the branched GAP product was investigated in DMSO and DMA as reported in Table VII. All the samples were obtained after 5 h at 120°C with the same cleaving agent concentration (CH_3OLi/PECH = 0.030) and using glycerol or EG as polyol. The values of M_e and [OH] determined for the samples prepared in DMSO are listed in Table VII along with the values measured for the DMA products. [OH] is the hydroxyl content in the polymer expressed in meq OH/g and is equal to ($1000/M_e$). The variation of [OH] versus the polyol proportion in the reaction is also plotted in Fig. 2 for the products obtained in DMSO and DMA.

As shown in Table VII and in Fig. 2, the hydroxyl content in the product is higher for the samples prepared in DMSO compared with DMA. Samples N 23

([OH] = 0.62), E 260 ([OH] = 0.59) and E 229 ([OH] = 0.40) obtained in DMSO with glycerol, EG and without polyol respectively have a higher hydroxyl content than Samples E 258 ([OH] = 0.37), E 161 ([OH] = 0.33) and E 257 ([OH] = 0.29) prepared in DMA with glycerol, EG and without polyol, respectively. The difference in the hydroxyl content observed between the DMSO and DMA products was noted in all cases: for reactions using polyols such as glycerol or EG in different proportions as well as for reactions carried out without polyol. Therefore, the branched GAP samples obtained in DMSO contain relatively more OH groups than their counterparts prepared in DMA with similar experimental conditions; this has a noticeable effect on the curing reactions of these samples with isocyanates and the mechanical properties of the energetic formulations, as reported in Refs. 32-34.

The results obtained in DMSO for Samples N 17 ([OH] = 0.50) and E 259 [OH] = 0.50) prepared respectively with glycerol and EG using a low concentration (polyol/PECH = 0.25) and for Samples N 23 ([OH] = 0.62) and E 260 ([OH] = 0.59) prepared also with glycerol and EG, respectively, but with a high concentration (polyol/PECH = 1.0), show that in a given solvent, the glycerol or EG concentration had a more significant effect on the hydroxyl content of the product than the type of polyol used in the reaction. The effect of the polyol concentration on the properties of the GAP product will be discussed in the next section.

3.8 Effect of Polyol Concentration

The effect of the polyol concentration on the degradation and the hydroxyl content of the branched GAP product was investigated for two different polyols (TMP, PE), as reported in Table VIII. All the samples were obtained in DMSO after 16 h at 120°C with the same cleaving agent concentration (CH_3OLi/PECH = 0.03). The values of M_W, M_n and [OH] determined for various samples prepared with TMP and PE at

different polyol proportions are listed in Table VIII. The variations of M_W and [OH] versus the polyol concentration are also plotted in Fig. 3 and Fig. 4, respectively.

The results of Table VIII and Fig. 3 show that the values of M_W and M_e for the branched GAP samples are generally reduced when the polyol concentration is increased in the reaction mixture. This is an indication that the polyol co-reagent participates to some degree in the degradation mechanism by promoting the scission of polymeric chains and/or enhancing the reactivity of the cleaving agent thus causing a further reduction in the MW of the GAP product. However, in some cases, the MW is lowered gradually to a certain level and then no significant MW reduction is noted when the polyol concentration is increased furthermore as observed for Samples N 123 and N 75 prepared with TMP, when the polyol proportion (TMP/PECH) exceeded a ratio of 0.10. This phenomenon could be explained by some cross-linking reactions involving the polyol and which become predominant at high polyol concentrations.

The results of Table VIII and Fig. 4 show also that the hydroxyl content of the branched GAP product increases with the polyol concentration. This is an indication that more OH groups are grafted into the GAP molecular structure as the polyol proportion is increased in the reaction mixture. Depending on the type of polyol used and its concentration in the reaction, additional primary and secondary alcohols (originating from the polyol) are thus incorporated into the molecular structure of the GAP binder enhancing thus significantly the mechanical properties of the energetic formulations, as reported in Refs. 34-36.

3.9 Effect of Polyol Type

The effect of the type of polyol used in the reaction on the properties of the branched GAP product was investigated for various polyols in different solvents (DMA, DMSO) and using CH_3OLi and NaOH as cleaving agents.

The values of M_N, M_e, f and η determined for the GAP samples prepared in DMA with different polyols are listed in Table IX. All the samples were obtained after 16 h at 120°C using a similar weight ratio (cleaving agent/PECH) of 0.043. The following polyols were tested in DMA: TMP, glycerol, EG, HT, PEG (MW 400) and PEG (MW 600). The weight ratio (polyol/PECH) used in the reactions was 0.25-0.50 for all the samples. As shown in Table IX, for the GAP samples obtained in DMA, the values of M_N varied in the range 4000-27,900, the values of M_e were in the range 1480-3357, the functionality was between 2.7 and 8.3 and the viscosity at 25°C varied between 30,000 cP and 400,000 cP depending on the system polyol/cleaving agent used in the reaction.

The values of M_N, M_e, f and η determined for the GAP samples prepared in DMSO with various polyols and mixtures of polyols are listed in Table X. All the samples were obtained after 16 h at 120°C using a weight ratio (cleaving agent/PECH) of 0.030 for CH_3OLi and 0.045 for NaOH. The following polyols were tested in DMSO: TMP, PE, DPE, HT, glycerol, EG, PEG (MW 600), PVA, sucrose and GAP. The weight ratio (polyol/PECH) used in the reactions was 0.15-0.25 for all the polyols tested except PVA; a lower ratio of 0.005 was used for PVA to prevent the gelling that occurred at higher PVA concentrations. As shown in Table X, for the GAP samples prepared in DMSO the values of M_N varied in the range 3620-16,700, the values of M_e

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were in the range 1247-2689, the functionality was between 2.8 and 6.2 and the viscosity at 25°C varied between 29,000 cP and 162,000 cP depending on the types of polyol and cleaving agent used in the reaction.

The results in Table X show also that a branched GAP sample prepared using a blend of two polyols will have for the MW, functionality and viscosity intermediate values between those of the two samples synthesized each by using singly one of the two polyol components. For instance, Sample N 107 prepared with a polyol mixture (60 % PE - 40 % HT) had M_N, M_e, f and η values corresponding approximately to the sum of 60 % of those of Sample N 98 (obtained with PE) and 40 % of those of Sample N 116 (prepared with HT).

The effect of the type of polyols (or mixture of polyols) used in the synthesis of branched GAP on the mechanical properties of the energetic formulations are reported in Refs. 34-36. The results of Tables IX and X show that the properties of the branched GAP product can be modified and tailored to suit the desired application by the proper selection of the types of polyol and cleaving agent and by varying their relative proportions in the reaction mixture. The results in Tables IX and X show also that the values of f increase with M_N and η; the functionality-MW relationship will be discussed in another report (Ref. 27).

3.10 Effect of Sequence of Addition of Reactants

The effect of the sequence of addition of the reactants on the MW of the branched GAP product was investigated at 100°C and 120°C using respectively CH_3OLi and NaOH as cleaving agents.

The results of the branched GAP samples prepared at 100°C with a weight ratio (CH_3OLi/PECH) of 0.10 are reported in Table XI. The samples were obtained after 16 h in DMA and DMSO using respectively EG and glycerol as polyols; the weight ratio (polyol/PECH) was 1.0 for EG and 0.5 for glycerol. Samples E 125 (M_w = 9200), E 76 (M_w = 14,000) and E 124 (M_w = 25,000) were obtained in DMA in the same experimental conditions, except for the sequence of addition of the cleaving agent and the azide, and the time interval between the addition of these 2 reactants. Sample E 125 obtained when the cleaving agent was added 5 h before the azide had a much lower MW than Sample E 124 which was prepared by adding the cleaving agent 1 h after the azide. Samples E 127, E 126, E 122 and E 128 were all prepared in DMSO with similar synthesis parameters, except for the sequence and the time interval between the addition of the cleaving agent and the azide. Sample E 127, obtained when the azide and the cleaving agent were added together, had the lowest M_w (5200). Samples E 126 and E 122, prepared by adding the cleaving agent respectively 3 h before and 1 h after the azide had similar M_w (about 9300), whereas Sample E 128 synthesized by adding the cleaving agent 5 h after azide had the highest M_w (47,700).

The results of Table XI obtained in DMA and DMSO for the samples prepared at 100°C with CH_3OLi show that the branched GAP product generally has a lower MW when the cleaving agent is added before the azide. This is an indication that the alkyl groups ($-CH_2C\ell$) of PECH are involved in the degradation mechanism before the addition of NaN_3; the chain scission and MW reduction are thus achieved rapidly when the azide is not present in the reaction mixture. Once NaN_3 is added, the nucleophilic substitution begins and as the $-CH_2C\ell$ groups are gradually converted to CH_2N_3 groups, fewer $CH_2C\ell$ groups will become available to participate in the chain cleavage mechanism and the MW reduction will therefore proceed at a slower rate. If the cleaving agent is added before the azide, gelling could occur occasionally (as discussed in Section 2.4); on the other hand, products with relatively high MW will be

obtained if the cleaving agent is added long time (more than 3-4 h) after the azide. For this reason it is recommended to add the cleaving agent 1-2 h after the azide when the reaction is carried out at 100°C.

The results of the branched GAP samples prepared at 120°C with a weight ratio (NaOH/PECH) of 0.045 are reported in Table XII. The samples were obtained after 16 h in DMSO using glycerol, hexanetriol and TMP as polyols; in each case, two different procedures (A and B) were investigated for the sequence of addition of the reactants. In procedure A, the cleaving agent was added 15 min. before the azide, whereas in procedure B it was added 15 min after the azide. At 120°C, the reaction kinetics are faster than 100°C and for this reason, the time interval between the addition of the reactants is relatively short (15 min.) at 120°C compared with the interval (1-2 h) used for the reactions of 100°C presented in Table XI.

Samples N 71 (M_w = 9031) and N 73 (M_w = 9426) prepared according to procedures A and B, respectively, with a low TMP concentration (polyol/PECH = 0.15) had approximately the same MW. Therefore, when TMP was used as polyol, no significant difference was observed for the MW of the product whether the cleaving agent was added 15 min. before or after the azide. Samples N 70 (M_w = 12,770) and N 72 (M_w = 14,910) were both prepared with hexanetriol (polyol/PECH = 0.15) according to procedures A and B, respectively, whereas Samples N 67 (M_w = 32,400) and N 69 (M_w = 39,660) were both synthesized with glycerol (polyol/PECH = 0.25) according to procedures A and B, respectively. Consequently, for reactions involving hexanetriol and glycerol at low concentrations (polyol/PECH = 0.15-0.25) the GAP MW was about 20 % lower when procedure A was used instead of procedure B. The MW of the product was therefore lower when the cleaving agent was added before the azide as observed for reaction temperatures of 100°C. On the other hand, the results of Samples N 66 (M_w = 11,150) and N 68 (M_w = 9240) prepared both with glycerol

(polyol/PECH = 1.0) according to procedures A and B, respectively, indicate that at high glycerol concentration, the MW of the product was approximately 20 % higher when the cleaving agent was added before the azide.

The results of Table XII obtained for the system DMSO/NaOH show that at 120°C, the variation of the GAP MW with the sequence of addition of the reactants is dependent on the polyol type and its concentration in the reaction mixture. For reaction temperatures of 120°C, procedure B is adopted preferably to procedure A to prevent the gelling that could occur occasionally (as discussed in Section 2.4) when procedure A is used. Therefore, for reactions carried out at 120°C, it is recommended to add the cleaving agent approximately 15 min. after the azide.

4.0 CONCLUSIONS

Second generation branched GAP with variable and predetermined MW can be prepared in one step from the reaction of a solid rubbery PECH of high MW (~ 10^6) with NaN_3 and a basic cleaving agent (such as CH_3OLi or NaOH) in the presence of a polyol (such as TMP or glycerol) according to a novel degradation process developed at DREV. However, in this process the cleaving agent and/or the polyol are optional.

For reactions involving a cleaving agent, the MW of the branched GAP product varies within the range 1000-40,000 and the hydroxyl functionality is between 2 and 10. The MW and properties of the GAP product can be controlled and adjusted to suit the desired application by the proper selection of the types of cleaving agent and polyol and by varying their relative proportions in the reaction mixture. Other parameters, such as reaction time and temperature, the solvent and sequence of addition of the reactants, have also a significant effect on the MW, viscosity and hydroxyl content of the product.

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The synthesis parameters are interdependent; the effect of a specific parameter on the properties of the branched GAP product is more or less significant depending on the other parameters and experimental conditions selected for the synthesis reaction.

Lower cleaving agent concentrations are required at a reaction temperature of 120°C to reach the same degradation rate obtained at 100°C with higher concentrations.

The chain cleavage and MW reduction of the polymer are achieved more rapidly in DMSO compared with the other polar organic solvents (DMA, DMF) investigated; the synthesis of branched GAP with relatively low M_w (about 10,000) and viscosity (approx. 40,000 cP at 25°C) is obtained in about 5 h at 120°C in DMSO.

The branched GAP products prepared in DMSO have a relatively higher hydroxyl content than their counterparts obtained in DMA with similar experimental conditions.

The MW of the branched GAP product is generally reduced when the concentration of cleaving agent and/or polyol is increased in the reaction mixture; the hydroxyl content of the product increases with the polyol concentration used for the synthesis reaction.

This versatile process which yields branched GAP products with tailored MW, M_e and viscosity values could provide greater flexibility in the optimization of the mechanical properties of energetic formulations.

This degradation process appears cost-effective since the reaction is achieved in a single step in a relatively short time period and requires a cheap commercially available rubbery PECH as the starting material.

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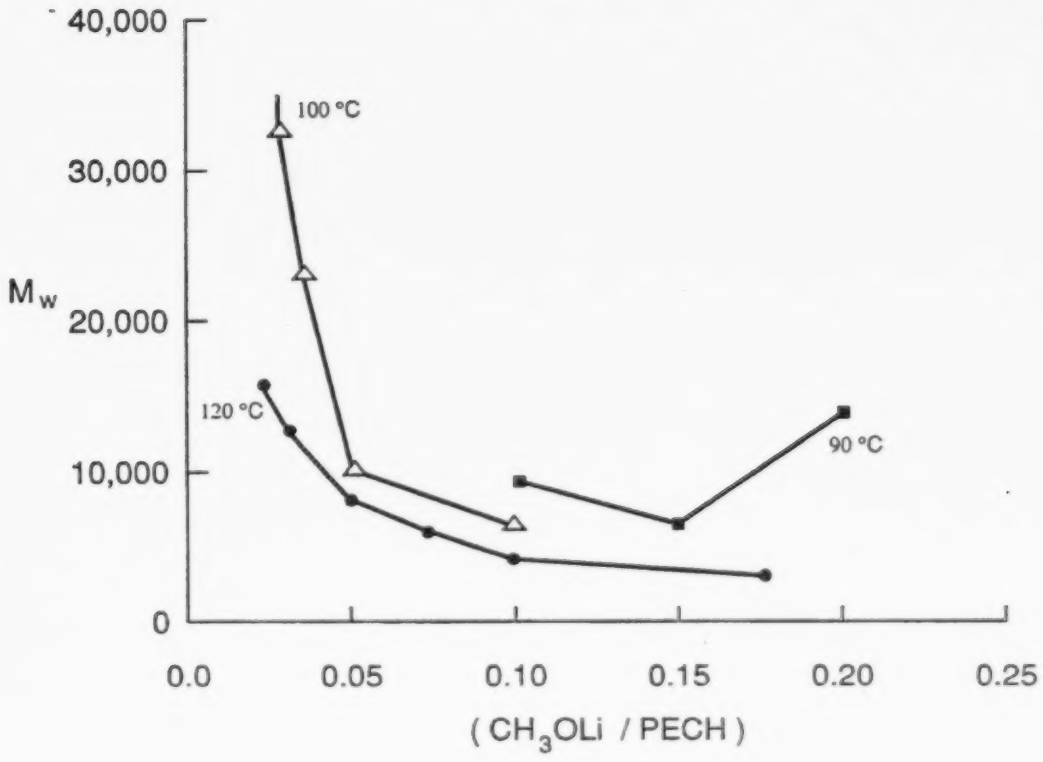

FIGURE 1 - Variation of M_w with CH_3OLi concentration for the system (DMSO/GLYCEROL) at different temperatures
120°C (reaction time = 5 h)
100°C (" " = 16 h)
90°C (" " = 32 h)

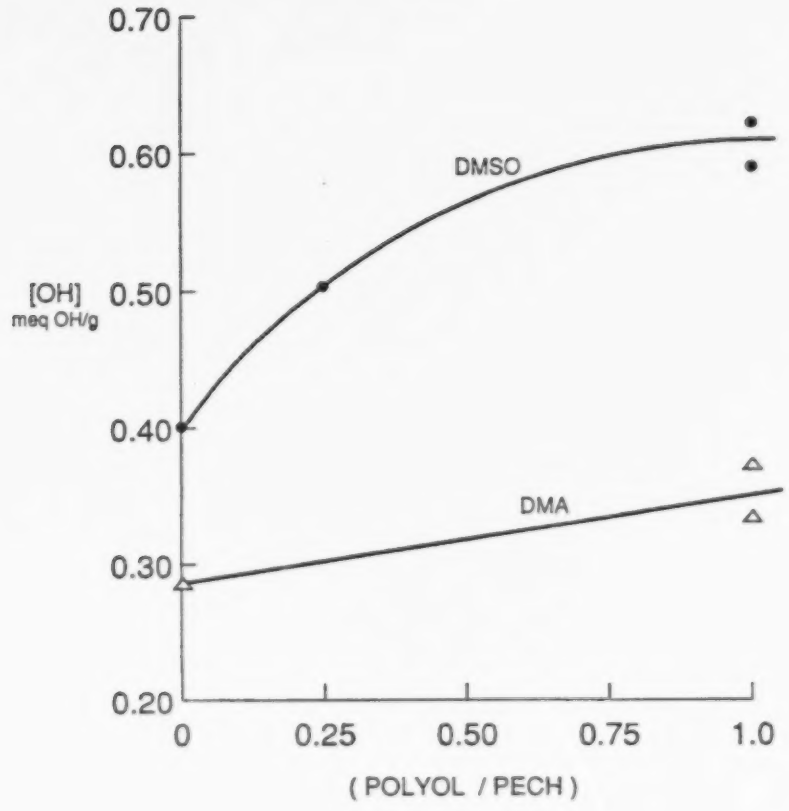

FIGURE 2 - Solvent effect on hydroxyl content in branched GAP product

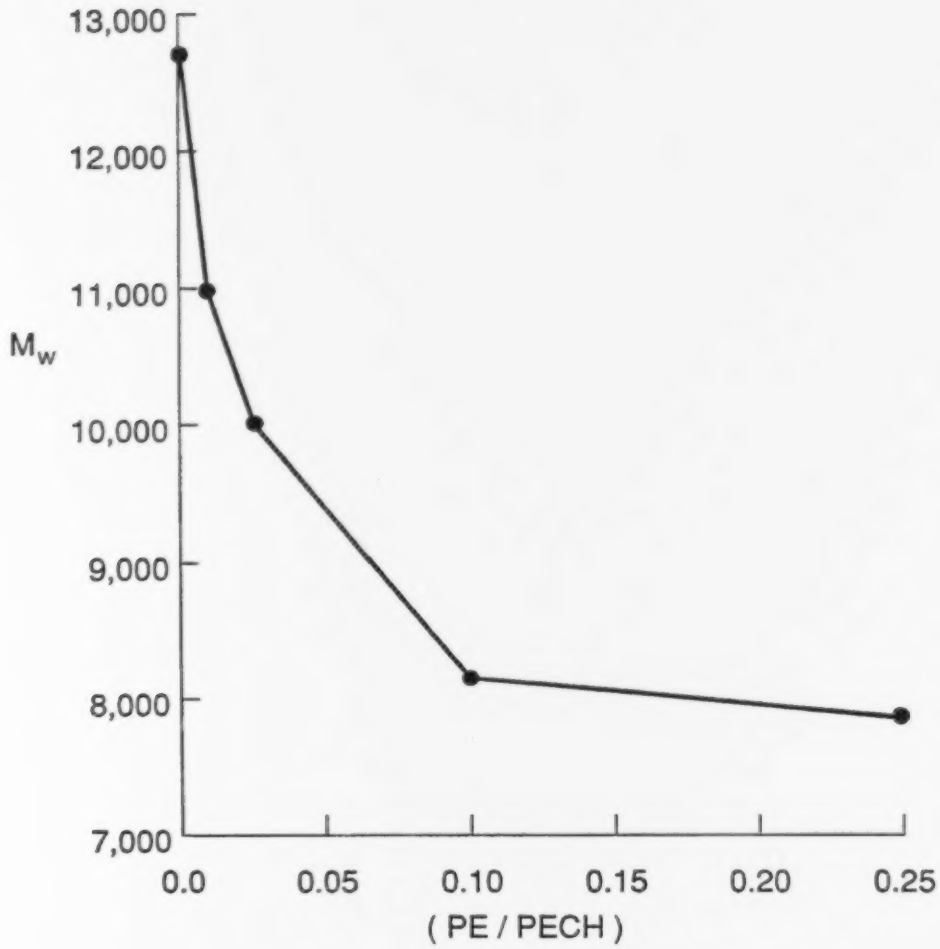

FIGURE 3 - Variation of M_w with PE concentration in DMSO

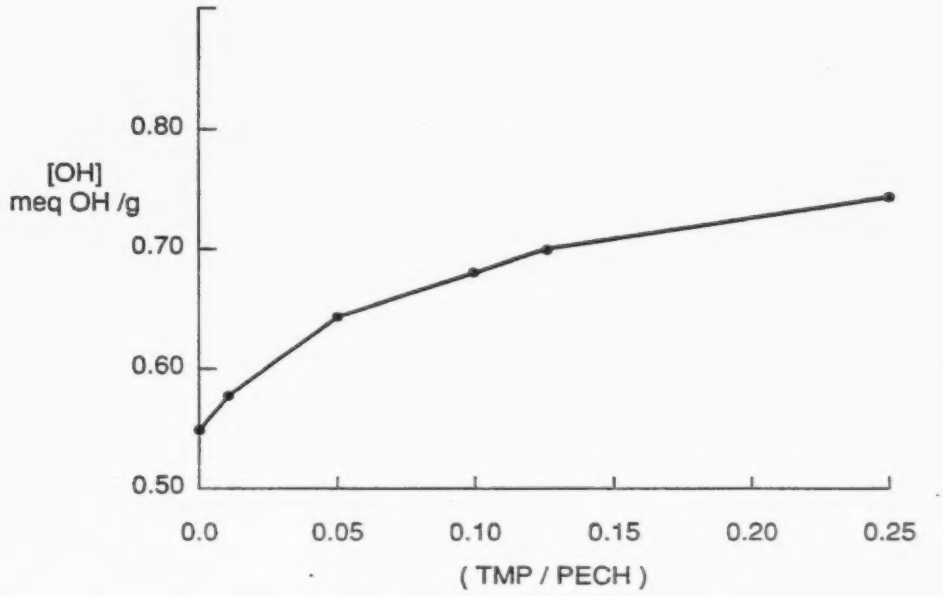

FIGURE 4 - Variation of hydroxyl content with TMP concentration in DMSO

TABLE I

Effect of reaction time on MW

Sample *	Solvent	Reaction time (h)	M_w
E148	DMSO	5	12,000
E156		16	8,500
E158		32	7,000
E174	DMA	5	11,500
N33		16	9,000
E171	DMF	5	12,000
E169-2		16	9,500

* samples prepared at 120°C with (CH_3OLi/PECH) = 0.041 and (glycerol/PECH) = 0.25

TABLE II

Effect of reaction temperature on MW

Sample *	Solvent	Reaction		Cleaving Agent	(Cleaving agent / PECH)	M_w
		Temperature °C	time (h)			
E55	DMA	100	16	NaOH	0.05	43,400
N48		120	"	"	"	14,800
E241	DMSO	90	16	CH_3OLi	0.03	20,700
E242		100	"		"	15,500
N12		120	"		"	13,500
E130	DMSO	100	16	CH_3OLi	0.10	4,800
E238		120	"		"	2,600
E153	DMSO	90	32	CH_3OLi	0.10	6,700
E131		100	"		"	4,700

* samples prepared with (glycerol/PECH) = 1.0

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TABLE III

Effect of cleaving agent type on MW

Sample	REACTION			Polyol	Polyol / PECH	Cleaving Agent		[Cleaving Agent]	M_w
	Solvent	Temperature °C	Time (h)			Type	MW		
N65	DMSO	120	16	TMP	0.25	CH_3OLi	38	0.073	9535
N146					"	NaOH	40	0.070	9219
E211					"	CH_3ONa	54	0.086	19,000
N55	DMA	120	16	TMP	0.25	CH_3OLi	38	0.10	9100
E178					"	NaOH	40	0.10	15,400
N147					"	CH_3ONa	54	0.10	55,100
E27	DMF	100	32	EG	1.0	NaOH	40	0.35	10,700
E24					"	K Ter Butoxide	112	0.35	13,000
E25					"	C_2H_5ONa	68	0.35	28,000

TABLE I

Effect of reaction time on MW

Sample *	Solvent	Reaction time (h)	M_w
E148	DMSO	5	12,000
E156		16	8,500
E158		32	7,000
E174	DMA	5	11,500
N33		16	9,000
E171	DMF	5	12,000
E169-2		16	9,500

* samples prepared at 120°C with (CH_3OLi/PECH) = 0.041 and (glycerol/PECH) = 0.25

TABLE II

Effect of reaction temperature on MW

Sample *	Solvent	Reaction		Cleaving Agent	$\left(\frac{\text{Cleaving agent}}{\text{PECH}}\right)$	M_w
		Temperature °C	time (h)			
E55	DMA	100	16	NaOH	0.05	43,400
N48		120	"	"	"	14,800
E241	DMSO	90	16	CH_3OLi	0.03	20,700
E242		100	"		"	15,500
N12		120	"		"	13,500
E130	DMSO	100	16	CH_3CLi	0.10	4,800
E238		120	"		"	2,600
E153	DMSO	90	32	CH_3OLi	0.10	6,700
E131		100	"		"	4,700

* samples prepared with (glycerol/PECH) = 1.0

TABLE III

Effect of cleaving agent type on MW

Sample #	REACTION			Polyol	$\left(\frac{\text{Polyol}}{\text{PECH}}\right)$	Cleaving Agent		[Cleaving Agent]	M_w
	Solvent	Temperature °C	Time (h)			Type	MW		
N65	DMSO	120	16	TMP	0.25	CH_3OLi	38	0.073	9535
N146					"	NaOH	40	0.070	9219
E211					"	CH_3ONa	54	0.086	19,000
N55	DMA	120	16	TMP	0.25	CH_3OLi	38	0.10	9100
E178					"	NaOH	40	0.10	15,400
N147					"	CH_3ONa	54	0.10	55,100
E27	DMF	100	32	EG	1.0	NaOH	40	0.35	10,700
E24					"	K Ter Butoxide	112	0.35	13,000
E25					"	C_2H_5ONa	68	0.35	28,000

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TABLE IV

Effect of cleaving agent concentration on MW and viscosity

Sample	REACTION			Polyol	$\left(\frac{CH_3OL_2}{PECH}\right)$	Viscosity (25°C) cP	M_w
	Solvent	Temperature °C	Time (h)				
E236	DMSO	120	5	Glycerol	0.02	66,000	16,300
N16					0.03	50,000	12,400
E152					0.05	34,000	8300
E140					0.075	29,000	6400
E136					0.10	24,000	4500
E235					0.175	18,000	2800
E107	DMSO	100	16	Glycerol	0.03	135,000	33,000
E106					0.04	97,000	24,000
E90					0.05	40,000	10,000
E88					0.10	27,000	5800
E142	DMSO	90	32	Glycerol	0.10	35,000	8800
E138					0.15	26,000	5300
E139					0.20	54,000	13,400
N106	DMSO	120	5	TMP	0.0125	133,000	32,700
N105					0.020	78,000	19,300
N104					0.030	68,000	16,900

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TABLE IV (Continued)

Sample	REACTION			Polyol*	$\left(\frac{CH_3OL}{PECH}\right)$	Viscosity (25°C) cP	M_w
	Solvent	Temperature °C	Time (h)				
E105 E104 E100-1	DMSO/NMP 70% 30%	100	16	Glycerol	0.03 0.05 0.10	230,000 67,000 40,000	46,100 16,400 10,000
E47 E76 E77	DMA	100	16	EG	0.05 0.10 0.15	125,000 52,000 100,000	30,800 13,000 25,200
E66 E71 E72	DMA	100	32	Glycerol	0.05 0.10 0.15	114,000 40,000 90,000	28,000 10,000 22,500

*$\left(\frac{\text{polyol}}{\text{PECH}}\right)$ = 0.15-0.10 for glycerol and EG
= 0.25 for TMP

TABLE IV

Effect of cleaving agent concentration on MW and viscosity

Sample	REACTION			Polyol	$\left(\frac{CH_3OLi}{PECH}\right)$	Viscosity (25°C) cP	M_w
	Solvent	Temperature °C	Time (h)				
E236	DMSO	120	5	Glycerol	0.02	66,000	16,300
N16					0.03	50,000	12,400
E152					0.05	34,000	8300
E140					0.075	29,000	6400
E136					0.10	24,000	4500
E235					0.175	18,000	2800
E107	DMSO	100	16	Glycerol	0.03	135,000	33,000
E106					0.04	97,000	24,000
E90					0.05	40,000	10,000
E88					0.10	27,000	5800
E142	DMSO	90	32	Glycerol	0.10	35,000	8800
E138					0.15	26,000	5300
E139					0.20	54,000	13,400
N106	DMSO	120	5	TMP	0.0125	133,000	32,700
N105					0.020	78,000	19,300
N104					0.030	68,000	16,900

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TABLE IV (Continued)

Sample	REACTION			Polyol *	$\left(\frac{CH_3OLi}{PECH}\right)$	Viscosity (25°C) cP	M_w
	Solvent	Temperature °C	Time (h)				
E105	DMSO/NMP	100	16	Glycerol	0.03	230,000	46,100
E104	70% 30%				0.05	67,000	16,400
E100-1					0.10	40,000	10,000
E47	DMA	100	16	EG	0.05	125,000	30,800
E76					0.10	52,000	13,000
E77					0.15	100,000	25,200
E66	DMA	100	32	Glycerol	0.05	114,000	28,000
E71					0.10	40,000	10,000
E72					0.15	90,000	22,500

* $\left(\frac{\text{polyol}}{\text{PECH}}\right)$ = 0.15-0.10 for glycerol and EG
= 0.25 for TMP

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TABLE V
Effect of solvent type on degradation

POLYOL/CLEAVING AGENT	REACTION SOLVENT					
	DMSO		DMA		DMF	
EG / NaOH	7800	E181	14,300	E173	62,000	E168
EG / CH_3OLi	6100	E237	19,100	N36	18,000	E245
Glycerol / NaOH	39,700	N69	63,600	N37	59,400	E246
Glycerol / CH_3OLi	7600	N-09-2	8400	E175	8500	E169
	M_w	+Sample	M_w	+Sample	M_w	+Sample

+ All samples were obtained after 16 h at 120°C
* (Polyol/PECH) = 0.25, (cleaving agent/PECH) = 0.043

TABLE VI
Effect of solvent concentration on degradation

Sample	Polyol	$\left(\frac{CH_3OLi}{PECH}\right)$	$\left(\frac{DMA}{PECH}\right)$	M_w
N36	EG	0.045	8	19,100
E244	"	"	16	14,400
E175	Glycerol	0.042	8	10,000
E243	"	"	16	9000

* All GAP samples were obtained at 120°C after 16 h in DMA with (Polyol/PECH) = 0.25

TABLE VII

Solvent effect on hydroxyl content in product

Sample	Reaction Solvent	Polyol	$\left(\frac{Polyol}{PECH}\right)$	M_n	[OH] meq OH/g
E229	DMSO	NONE	0	2487	0.40
N17		Glycerol	0.25	1994	0.50
E259		EG	"	1995	0.50
N23		Glycerol	1.0	1610	0.62
E260		EG	"	1696	0.59
E257	DMA	NONE	0	3500	0.29
E258		Glycerol	1.0	2700	0.37
E161		EG	1.0	3000	0.33

* All samples were obtained after 5 h at 120°C with (CH_3OLi/PECH) = 0.030

TABLE V
Effect of solvent type on degradation

POLYOL/CLEAVING AGENT	REACTION SOLVENT					
	DMSO		DMA		DMF	
EG / NaOH	7800	E181	14,300	E173	62,000	E168
EG / CH_3OLi	6100	E237	19,100	N36	18,000	E245
Glycerol / NaOH	39,700	N69	63,600	N37	59,400	E246
Glycerol / CH_3OLi	7600	N-09-2	8400	E175	8500	E169
	M_w	+Sample	M_w	+Sample	M_w	+Sample

+ All samples were obtained after 16 h at 120°C
* (Polyol/PECH) = 0.25, (cleaving agent/PECH) = 0.043

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TABLE VI
Effect of solvent concentration on degradation

Sample	Polyol	$\left(\frac{CH_3OLi}{PECH}\right)$	$\left(\frac{DMA}{PECH}\right)$	M_w
N36	EG	0.045	8	19,100
E244	"	"	16	14,400
E175	Glycerol	0.042	8	10,000
E243	"	"	16	9000

* All GAP samples were obtained at 120°C after 16 h in DMA with (Polyol/PECH) = 0.25

TABLE VII

Solvent effect on hydroxyl content in product

Sample	Reaction Solvent	Polyol	$\left(\frac{Polyol}{PECH}\right)$	M_n	[OH] meq OH/g
E229	DMSO	NONE	0	2487	0.40
N17		Glycerol	0.25	1994	0.50
E259		EG	"	1995	0.50
N23		Glycerol	1.0	1610	0.62
E260		EG	"	1696	0.59
E257	DMA	NONE	0	3500	0.29
E258		Glycerol	1.0	2700	0.37
E161		EG	1.0	3000	0.33

* All samples were obtained after 5 h at 120°C with (CH_3OLi/PECH) = 0.030

TABLE VIII

Effect of polyol concentration on degradation & hydroxyl content

*Sample	Polyol	$\left(\frac{\text{Polyol}}{\text{PECH}}\right)$	M_w	M_n	[OH] meq OH/g
N95	NONE	0	12,800	1810	0.55
N83	TMP	0.012	10,900	1730	0.58
N81		0.05	10,600	1551	0.64
N79		0.10	8300	1478	0.68
N123		0.125	8800	1438	0.70
N75		0.25	9500	1358	0.74
N93	PE	0.0075	11,000	1610	0.62
N92		0.025	10,000	1570	0.64
N91		0.10	8300	1418	0.70
N90		0.25	7800	1338	0.75

* All samples were prepared in DMSO for 16 h at 120°C with (CH_3OLi/PECH) = 0.030

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TABLE IX

Effect of polyol type in DMA

*Sample	Cleaving Agent	Polyol	M_N	M_e	f_i	Viscosity (25°C) cP
N76	NaOH	TMP	6740	1925	3.5	54,000
N32		EG	6700	2030	3.3	60,000
E177		PEG (MW 600)	7750	2213	3.5	66,000
E176		Hexanetriol	10,900	2667	4.1	81,000
N37		Glycerol	27,900	3357	8.3	400,000
N33	CH_3OLi	Glycerol	4000	1480	2.7	30,000
N55		TMP	4800	1660	2.9	34,000
N39		PEG (MW 400)	5200	1730	3.0	40,000
N56		PEG (MW 600)	6050	1890	3.2	48,000
N54		Hexanetriol	8300	2380	3.5	57,000
N36		EG	9880	2670	3.7	70,000

* All samples were obtained in DMA after 16 h at 120°C with (cleaving agent/PECH) = 0.043 and (Polyol/PECH) = 0.25-0.50

TABLE VIII

Effect of polyol concentration on degradation & hydroxyl content

*Sample	Polyol	$\left(\frac{\text{Polyol}}{\text{PECH}}\right)$	M_w	M_n	[OH] meq OH/g
N95	NONE	0	12,800	1810	0.55
N83	TMP	0.012	10,900	1730	0.58
N81		0.05	10,600	1551	0.64
N79		0.10	8300	1478	0.68
N123		0.125	8800	1438	0.70
N75		0.25	9500	1358	0.74
N93	PE	0.0075	11,000	1610	0.62
N92		0.025	10,000	1570	0.64
N91		0.10	8300	1418	0.70
N90		0.25	7800	1338	0.75

* All samples were prepared in DMSO for 16 h at 120°C with (CH_3OLi/PECH) = 0.030

TABLE IX

Effect of polyol type in DMA

*Sample	Cleaving Agent	Polyol	M_N	M_c	f	Viscosity (25°C) cP
N76	NaOH	TMP	6740	1925	3.5	54,000
N32		EG	6700	2030	3.3	60,000
E177		PEG (MW 600)	7750	2213	3.5	66,000
E176		Hexanetriol	10,900	2667	4.1	81,000
N37		Glycerol	27,900	3357	8.3	400,000
N33	CH_3OLi	Glycerol	4000	1480	2.7	30,000
N55		TMP	4800	1660	2.9	34,000
N39		PEG (MW 400)	5200	1730	3.0	40,000
N56		PEG (MW 600)	6050	1890	3.2	48,000
N54		Hexanetriol	8300	2380	3.5	57,000
N36		EG	9880	2670	3.7	70,000

* All samples were obtained in DMA after 16 h at 120°C with (cleaving agent/PECH) = 0.043 and (Polyol/PECH) = 0.25-0.50

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TABLE X

Effect of polyol type in DMSO

*Sample	Cleaving Agent	Polyol	M_N	M_w	ξ	Viscosity (25°C) cP
N98	CH_3OLi	PE	4000	1338	3..0	38,000
N107		PE(60%)/HT(40%)	4600	1478	3.1	37,000
N112		TMP(60%)/PEG600(40%)	5050	1530	3.3	39,000
N116		HT	4544	1548	2.9	40,000
N111		PE(60%)/PEG600(40%)	5350	1572	3.4	39,000
N118		DPE	5240	1415	3.7	35,000
N65		TMP	5000	1358	3.7	44,000
N110		PEG (MW600)	5500	1959	2.8	41,000
E230		GAP(50%)/TMP(50%)	7710	1977	3.9	57,000
E224		GAP	10,900	2370	4.6	162,000
N140		PVA (80% hyd)	8340	2033	4.1	67,000
E213		Sucrose	9200	1728	5.3	127,000
E181	NaOH	EG	3620	1247	2.9	29,000
N73		TMP	4310	1348	3.2	44,000
N72		Hexanetriol	6460	1576	4.1	77,000
N69		Glycerol	16,700	2689	6.2	134,000

* All samples were obtained in DMSO after 16 h at 120°C
(cleaving agent/PECH) = 0.030 for CH_3OLi and 0.045 for NaOH
(Polyol/PECH) = 0.15-0.25 for all polyols except PVA
= 0.005 for PVA

TABLE XI

Effect of sequence of addition of reactants at 100°C

*Sample	Reaction Solvent	Polyol	M_w	Addition of Cleaving Agent
E124	DMA	EG	25,000	1 h after azide
E76		"	14,000	2 h before azide
E125		"	9200	5 h before azide
E128	DMSO	Glycerol	47,700	5 h after azide
E122		"	9100	1 h after azide
E126		"	9500	3 h before azide
E127		"	5200	with azide

* All samples were obtained after 16 h at 100°C with (CH_3OLi/PECH) = 0.10 (Polyol/PECH) = 1.0 for EG and 0.5 for glycerol

TABLE XII

Effect of sequence of addition of reactants at 120°C

*Sample	Polyol	$\left(\frac{\text{Polyol}}{\text{PECH}}\right)$	M_w	Procedure
N71	TMP	0.15	9031	A
N73		"	9426	B
N70	Hexanetriol	0.15	12,770	A
N72		"	14,910	B
N66	Glycerol	1.0	11,150	A
N68		"	9240	B
N67		0.25	32,400	A
N69		"	39,660	B

* All samples were prepared in DMSO for 16 h at 120°C with (NaOH/PECH) = 0.045

Procedure A : Cleaving agent added 15 min. before azide
Procedure B : " " " " after azide

TABLE X

Effect of polyol type in DMSO

*Sample	Cleaving Agent	Polyol	M_N	M_o	f	Viscosity (25°C) cP
N98	CH_3OLi	PE	4000	1338	3..0	38,000
N107		PE(60%)/HT(40%)	4600	1478	3.1	37,000
N112		TMP(60%)/PEG600(40%)	5050	1530	3.3	39,000
N116		HT	4544	1548	2.9	40,000
N111		PE(60%)/PEG600(40%)	5350	1572	3.4	39,000
N118		DPE	5240	1415	3.7	35,000
N65		TMP	5000	1358	3.7	44,000
N110		PEG (MW600)	5500	1959	2.8	41,000
E230		GAP(50%)/TMP(50%)	7710	1977	3.9	57,000
E224		GAP	10,900	2370	4.6	162,000
N140		PVA (80% hyd)	8340	2033	4.1	67,000
E213		Sucrose	9200	1728	5.3	127,000
E181	NaOH	EG	3620	1247	2.9	29,000
N73		TMP	4310	1348	3.2	44,000
N72		Hexanetriol	6460	1576	4.1	77,000
N69		Glycerol	16,700	2689	6.2	134,000

* All samples were obtained in DMSO after 16 h at 120°C
(cleaving agent/PECH) = 0.030 for CH_3OLi and 0.045 for NaOH
(Polyol/PECH) = 0.15-0.25 for all polyols except PVA
= 0.005 for PVA

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TABLE XI

Effect of sequence of addition of reactants at 100°C

*Sample	Reaction Solvent	Polyol	M_w	Addition of Cleaving Agent
E124	DMA	EG	25,000	1 h after azide
E76		"	14,000	2 h before azide
E125		"	9200	5 h before azide
E128	DMSO	Glycerol	47,700	5 h after azide
E122		"	9100	1 h after azide
E126		"	9500	3 h before azide
E127		"	5200	with azide

* All samples were obtained after 16 h at 100°C with (CH_3OLi/PECH) = 0.10
(Polyol/PECH) = 1.0 for EG and 0.5 for glycerol

TABLE XII

Effect of sequence of addition of reactants at 120°C

*Sample	Polyol	$\left(\frac{\text{Polyol}}{\text{PECH}}\right)$	M_w	Procedure
N71	TMP	0.15	9031	A
N73		"	9426	B
N70	Hexanetriol	0.15	12,770	A
N72		"	14,910	B
N66	Glycerol	1.0	11,150	A
N68		"	9240	B
N67		0.25	32,400	A
N69		"	39,660	B

* All samples were prepared in DMSO for 16 h at 120°C with (NaOH/PECH) = 0.045

Procedure A : Cleaving agent added 15 min. before azide
Procedure B : " " " " after azide

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Second generation branched Glycidyl Azide Polymer (GAP) is prepared according to a novel single step degradation process developed at DREV by reacting a high molecular weight (MW ~ 10^6) commercial rubbery polyepichlorohydrin (PECH) with sodium azide and a basic cleaving agent in the presence of a polyol for a few hours at elevated temperature in a polar organic solvent; however, in this process, the cleaving agent and/or the polyol are optional. For reactions involving a cleaving agent, the hydroxyl functionality of the GAP product is between 2 and 10 and the MW may be controlled and predetermined in the MW range 1000-40,000 by varying the concentration of cleaving agent in the reaction mixture. For reactions without a cleaving agent, the MW of the product is between 40,000 and 200,000 and the functionality is equal to, or above 10. The effect of some reaction parameters on the properties (MW, viscosity, hydroxyl content and functionality) of the branched GAP product was studied; the synthesis parameters investigated are the reaction time and temperature, the type and concentration of the cleaving agent, polyol and solvent as well as the sequence of addition of the reactants. Branched GAP with relatively low MW (~ 10,000) and viscosity (~ 40,000 cP at 25°C) can be synthesized in about 5 h at 120°C in dimethyl sulfoxide (DMSO) and the product thus obtained has a relatively higher hydroxyl content than its counterpart prepared in dimethyl acetamide (DMA) in similar experimental conditions.

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Synthesis
Degradation
Reaction parameters
Reactants
Polyol
Basic cleaving agent
Molecular Weight
Hydroxyl functionality
Viscosity
Polar Organic solvent

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